

The Specific Heats of the Phenyl Derivatives of Ethane and Some Related Compounds

A DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE
REQUIREMENTS FOR THE DEGREE OF DOCTOR
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THERMAL ENERGY STUDIES. I. PHENYL DERIVATIVES OF METHANE, ETHANE AND SOME RELATED COMPOUNDS

The importance of energy as a factor in chemistry has been recognized for a great many years and it has been a source of inspiration in many fields of research from the time of Thomsen and Berthelot down to the present day. Broadly speaking, if we knew the energy relationships of the molecule completely enough, we would be able to predict all the modes of chemical behavior.

One must admit, however, that it is very difficult to do chemical thinking in terms of energy on the basis of our present knowledge. Although we intuitively connect chemical behavior with structural formulas or the position of an element in the periodic table, we have never been able to draw a sufficiently intimate picture of the relation of energy to molecular and atomic structure, so that we can feel instinctively the role of energy in determining the course of a reaction, particularly when it involves complex molecules. What we need is a much more detailed knowledge of the energy associated with the different parts of the molecule and how it varies with temperature, environment and distortion or excitation of the molecule itself.

For answering these questions, one of the most valuable types of information is heat capacity data especially over a wide range of temperature. During the past fifteen years there has been a great deal of work done in securing information along this line, especially by Gibson,¹ Latimer,² Parks,² Giauque,³ Anderson⁴ and their associates, and by the group with which the present authors are connected.^{5,6} Especially within the last

¹ Gibson, Latimer and Parks, *J. Am. Chem. Soc.*, **42**, 1533 (1920); Gibson, Parks and Latimer, *ibid.*, **42**, 1542 (1920); Gibson and Giauque, *ibid.*, **45**, 93 (1923); Latimer, *ibid.*, **44**, 90 (1922); Latimer and Hoenshel, *ibid.*, **48**, 19 (1926); Latimer and Ahlberg, *ibid.*, **52**, 549 (1930).

² Parks, *ibid.*, **47**, 338 (1925); Parks and Kelley, *ibid.*, **47**, 2089 (1925); Parks and Anderson, *ibid.*, **48**, 1506 (1926); Parks and Huffman, *ibid.*, **48**, 2788 (1926); Parks, Kelley and Huffman, *ibid.*, **51**, 1969 (1929); Parks, Huffman and Thomas, *ibid.*, **52**, 1032 (1930); Huffman, Parks and Daniels, *ibid.*, **52**, 1549 (1930).

³ Giauque and Wiebe, *ibid.*, **50**, 101 (1928); **50**, 2193 (1928); **51**, 1441 (1929).

⁴ C. T. Anderson, *ibid.*, **52**, 2296, 2301, 2712, 2720 (1930).

⁵ Andrews, Lynn and Johnston, *ibid.*, **48**, 1274 (1926); Andrews, *ibid.*, **48**, 1287 (1926); Keesom and Andrews, *Verslag Konink. Akad. Wetens. Amsterdam*, **36**, 52 (1926); Andrews and Haworth, *J. Am. Chem. Soc.*, **50**, 2998 (1928); Andrews, *J. Franklin Inst.*, **206**, 285 (1928); Southard and Andrews, *ibid.*, **207**, 323 (1929); *ibid.*, **209**, 349 (1930).

⁶ Andrews, *Proc. Roy. Acad. Amsterdam*, **29**, 744 (1926); *Chemical Reviews*, **5**, 533 (1928); Bates and Andrews, *Proc. Nat. Acad. Sci.*, **14**, 124 (1928); Andrews and Southard, *Phys. Rev.*, **35**, 670 (1930).

year this field of research has been greatly stimulated by developments in the interpretation of Raman spectra. It appears that the frequencies in these spectra correspond to the fundamental vibrations in the molecule, and that from them one can calculate the energy associated with individual parts of the molecule.^{7,8,9,10,11}

In view of this an investigation has been undertaken to study the thermal energy in a number of series of complex molecules for the purpose of learning more about energy distribution within the molecule and its variation with temperature and molecular structure. Preparatory to this project methods for heat capacity measurement have been developed especially designed to permit the survey of a large number of compounds within a reasonable length of time.⁵ A preliminary survey has also been made of the general considerations of energy distribution in complex molecules.^{6,11}

In the present series of papers it is planned to present the results of the experimental heat capacity measurements, followed by a discussion of the theory of the heat capacity of complex molecules and a comparison of the experimental values with values calculated from Raman spectra. This paper gives the data obtained from the phenyl derivatives of methane and ethane which were selected as the first group for the thermal energy study. It was felt that a knowledge of heat capacities would be particularly valuable in a series such as this where, from the chemical standpoint, there appears to be a loosening of the carbon-carbon bond as the result of phenylation. These measurements are also valuable as a study of the specific heat of the benzene ring under varying conditions, and should furnish useful information for calculating the equilibrium constants of reactions involving phenylation.

The Method

The calibrated heat conduction method⁵ was selected because it offered the possibility of obtaining data of fair accuracy on a far larger number of compounds than would have been possible with the more precise but much slower method of intermittent electrical heating which has generally been used. The procedure consists essentially in passing heat into the substance through an insulating jacket across which a carefully controlled temperature head is maintained. The specific heat is calculated by comparing the rate of temperature rise with that of a standard substance heated under identical conditions. There is also the advantage with this method that no part of the temperature range is skipped in the observation and that any unusual thermal effects such as heats of transition are sure to be found.

⁷ Andrews, *ibid.*, **34**, 1626 (1929); **36**, 544 (1930).

⁸ Van Vleck, *Proc. Nat. Acad. Sci.*, **15**, 754 (1929).

⁹ Kettering, Shutts and Andrews, *Phys. Rev.*, **36**, 531 (1930).

¹⁰ R. C. Yates, *ibid.*, **36**, 555, 563 (1930).

¹¹ A. B. Lewis, *ibid.*, **36**, 568 (1930).

The actual experimental data are in the form of rise in temperature, Δ microvolts, which takes place in the time interval, t seconds, during which the temperature head across the insulating jacket is φ microvolts; θ is the mean temperature of the substance during observation. Consequently the quantity, Q , will be proportional to the heat capacity of the calorimeter and its contents, letting $Q = \varphi t / \Delta$. Table I gives the values of Q obtained at different temperatures in runs made at different times over a period of two months, illustrating the constancy of the calorimeter, after several improvements were made in the instrument as used by Andrews and Halloworth.⁶

Because of the lower effective heat capacity per unit volume of the substances used in this investigation as compared with previous investigations, an effort was made to increase the accuracy of the calorimeter by more careful control of small errors.

The chief source of error appeared to be the water frozen on the shield at low temperatures or present either as liquid or vapor above 0° . Two runs were made with the calorimeter empty and glass beads in the insulating space. One was made under the usual conditions, while for the other a drop of water was put inside the shield and vaporized before cooling the calorimeter. The large difference in the results showed the considerable effect that a small amount of water on the surfaces of the calorimeter can and shield had on the determinations. In order to dry the surfaces and the air in the insulating space, two short pieces of small copper tubing were soldered into holes drilled in the cover of the insulating jacket and a current of air from a drying train was passed through the calorimeter before each of the subsequent runs. These runs were all made without glass beads. A marked improvement in the results followed the use of this drying process.

In eliminating moisture from the calorimeter, another of the possible sources of error mentioned above was also removed. When the calorimeter was cooled, the gas taken into the insulating space was probably mostly oxygen from the liquid oxygen used for cooling. The thermal conductivities of oxygen and air differ enough to cause appreciable error if the composition of gas in the conduction space varies widely from run to run. By passing dry air through the calorimeter before and during the cooling process, it was insured that the gas in the conduction space was always the same.

Table I shows results obtained with 35.00 g. of triphenylmethane in four separate runs made over a period of two months. The procedure followed is described below. It is evident that the constants of the calorimeter did not change during this time. The average deviation of the individual results from the mean is about 0.35% or an extreme variation of 0.7%. This, together with comparisons made with data obtained by the

Nernst method, indicates an accuracy of about 1% for the method. It must be emphasized that results as consistent as those shown in the table are obtained only by constant attention to the details of manipulation. The absolute accuracy of the results depends, of course, on the precision of the values used for the standard substance. A detailed description of the exact procedure follows.

The Modified Procedure

The material to be measured was packed into the can and the top to the can put in place. In transferring the material into the calorimeter a little fine dust usually settled between the can and shield. This was blown out with compressed air. In fact, every effort was made to keep the inner surface of the shield and outer surface of the can scrupulously clean. Between runs these surfaces were always washed with hot benzene and with ether.

After placing the cover on the shield, a current was passed through the heating coil. Dry air was at the same time passed inside the shield. The heating was continued for ten minutes or until the temperature of the shield had reached about 60°. About five minutes after the heating current was turned off the calorimeter was placed in a gallon Dewar flask and 1.5 liters of liquid air added as rapidly as possible. The current of air through the conduction space was continued until the can and material had reached liquid air temperature.

In addition to a soda-lime tower and two wash bottles of sulfuric acid in the air drying train, a liquid air trap was used next in line to the calorimeter.

After shutting off the current of dry air, the procedure was essentially the same as described by Andrews and Haworth in the papers cited.⁵

Calibration of the Apparatus

Calibrations were made with naphthalene, triphenylmethane, toluene and hydroquinone. The triphenylmethane results were not as consistent as the others. Toluene was very good, but data were not available for higher temperatures. At temperatures both a little below and above the melting point of toluene this calibration gave results that were obviously erroneous. Two runs with hydroquinone gave very consistent results. Four runs with naphthalene were considered the most satisfactory and, since data on the heat capacity were available from several sources, that compound was chosen as the standard. The other compounds on which several runs were made served as a check on the accuracy of the method with different weights of material in the calorimeter.

Dr. R. F. Deese, Jr.,¹² very kindly supplied data on naphthalene covering the temperature range from 90 to 300°K. These results were obtained with a Nernst type calorimeter. Huffman, Parks and Daniels² have recently published a paper giving results on naphthalene over the same range. Andrews, Lynn and Johnston⁵ have given data for higher temperatures and the "International Critical Tables" give an equation for the specific heat over the range of -130° to the melting point. The values used for the heat capacity of naphthalene represent a combination of these data.

Runs were made on 30, 35, 40 and 45 g. of naphthalene and the resulting Q 's were plotted against the heat capacities for these weights at seventeen temperatures between 100 and 345°K. Only a few of the points were more than 0.5% from the best straight lines drawn through the four results for each temperature.

Standards of Measurement.—The temperature scale used in these

¹² Deese, private communication.

TABLE I

VALUES OF Q OBTAINED WITH 35.00 GRAMS OF TRIPHENYLMETHANE				
Microvolts below $^{\circ}\text{C}$.	Jan. 30	Feb. 21	March 6	March 30
5000	714	713	716	716
4500	868	865	867	869
4000	997	998	997	1001
3500	1116	1115	1114	1118
3000	1228	1224	1223	1227
2500	1330	1326	1327	1331
2000	1423	1422	1422	..
1500	1510	1513	1513	..
1000	1586	..	1590	..
500	1636	..	1638	..
0	1660	..	1664	..

measurements is that established by Southard⁵ and is based on the e. m. f. of several constantan-copper thermocouples calibrated at fifteen different temperatures against two platinum resistance thermometers made by the Leeds and Northrup Company and calibrated by the Bureau of Standards (L. and N., Nos. 128,016, 137,184 and B. of S., Nos. 2736, 312). The accuracy of this scale was amply sufficient for the purpose. The potentiometer, standard resistances and general method of electrical measurement are the same as previously used by Southard and Andrews.⁵

Preparation of Materials

The polyphenyl hydrocarbons desired for this work were either unobtainable or rather costly, making it necessary to prepare the greater number of them. It was thought desirable to have about two hundred grams of each of the purified products, and, due to the shrinkage of the materials in the several steps of the preparations and purifications, working on a fairly large scale was essential.

Technical grades of such comparatively inexpensive starting materials as benzene, bromobenzene, benzoyl chloride, benzyl chloride and benzaldehyde were obtained in rather large quantities and purified. The hydrocarbons were all built up from these simple compounds. Since such intermediates as benzophenone, diphenylbromomethane, triphenylchloromethane and others could each be used in getting several different hydrocarbons, these were prepared in quantities of several kilograms. The preparation and properties of the intermediates are well known and will not be described further here except in cases where specific heat determinations have been made.

Compounds of the requisite purity for specific heat determinations are somewhat difficult to obtain. It is highly desirable that the mole percentage of impurities should not be more than one- or two-tenths where measurements are to be made in the region of the melting point of the eutectic formed between compound and impurity. But since the specific heats of related organic compounds do not differ greatly, 2% of impurities may be present and not seriously affect the results obtained on the liquid or on the solid well below the point of fusion.

Recrystallizations were carried out in the usual manner. Solids were air dried and also dried in a vacuum desiccator from one to two weeks.

The column used in the fractional distillations was 60 cm. long and was filled with 5-mm. glass tubing cut in lengths about equal to the diameter. Heat loss from the column was diminished by a high-vacuum jacket. This insulation was sufficient to

permit distillations to be made at 125 to 150° without applying any heat to the column.

In all cases the distillations were carried out at reduced pressure so that the distillates came over at less than 130°. Dry carbon dioxide was passed in through the capillary in the distilling flask during all of the distillation.

A set of Anschütz thermometers was used for determining melting and boiling points. These were carefully checked against a new set of Bureau of Standards thermometers (B. S. Nos. 47,613 and 47,615).

Time-temperature freezing curves were made except in a few cases; these were taken as the final criterion of purity of the compounds.¹³

The record of source, method of preparation and of purification for the individual compounds is presented in the accompanying table. In the column headed "Source" the figures refer to the literature references which describe the source and method. "E. K. Co." refers to the Eastman Kodak Co.'s standard products.

In the column headed "Purification" the following notation is used: D, ordinary distillation; Ca, distillation from the column described above; S. D., steam distillation; Ca, recrystallization from alcohol; Cb, recrystallization from benzene; Ca_xb_y, recrystallization from *x* parts alcohol, *y* parts benzene.

Under "Melting point," "M. T." refers to the melting point determined in the ordinary way with a thermometer. "T. C." is the freezing point determined with a thermocouple. Under "Lit." are given the figures from the "International Critical Tables" (I) and from Beilstein's "Handbuch" (B).

Heat Capacities

Heat Capacities of the Phenyl Substituted Methanes.—The results of measurements on the four phenylmethanes are presented in Table III and Fig. 1.

TABLE III
MOLAL HEAT CAPACITIES OF THE PHENYL SUBSTITUTED METHANES

T, °K.	Calories per degree			
	Toluene	Diphenyl- methane	Triphenyl- methane	Tetraphenyl- methane
101.9	14.9	21.1	27.8	33.9
126.1	16.5	24.4	32.0	39.4
147.4	18.4	27.3	36.0	44.7
166.7	20.3	30.4	39.7	49.6
	Liquid			
184.4	31.7	33.2	43.4	54.7
201.1	32.2	36.2	47.1	59.1
216.8	32.6	39.3	50.6	63.0
231.7	33.1	41.7	53.9	67.7
246.0	33.9	44.3	57.2	71.4
259.8	34.6	47.1	60.4	75.4
273.1	35.6	49.9	63.8	79.9
286.0	37.0	52.7	67.0	84.0
298.5	38.7	55.8	70.6	88.0
	Liquid			
310.7		65.6	74.2	92.2
322.6		66.0	77.4	96.4
334.3			80.3	100.2
345.7			82.7	103.8

¹³ Andrews, Kohman and Johnston, *J. Phys. Chem.*, **29**, 914 (1925).

TABLE II
 PREPARATION OF COMPOUNDS

Substance	Source	Purification	M. T.	Melting point, °C.		Boiling point, °C.	Estimated impurities, %
				T. C.	Lit.		
Toluene	E. K. Co.	De	...	-95.15	-95.1	...	0.1
Diphenylmethane	14	3D, 2Dc	25.0-25.1	25.15	I, 27	86-86 (1 mm.)	.1
Triphenylmethane	15	D, 3Ca, D	93.6-93.8	93.1	I, 92.5	...	...
Tetraphenylmethane	16	3Cb, D, 2Cb	283	...	I, 285	...	...
Ethylbenzene	Commercial	3Dc	...	-95.26	I, -92.8	...	.1
1,1-Diphenylethane	17	D, Dc	...	-25.9	...	101-101.5 (2 mm.)	...
1,2-Diphenylethane	18 D, Ca, D, Ca, D, Ca, Dc	51.2-51.4	50.8	I, 52.5	...	95-96 (1 mm.)	.3
1,1,1-Triphenylethane	19	5Ca	94.8-95.0	94.3	B, 95	...	.1
1,1,2-Triphenylethane	20	D, 4Ca	54.0-54.3	48.0	I, 54	...	...
1,1,1,2-Tetraphenylethane	21	Ca _b	143.5-143.7	141.1	B, 140-142	...	...
1,1,2,2-Tetraphenylethane	22	Cb, 2Cb _{2a}	211.4-211.7	210.4	I, 209	...	.5
Pentaphenylethane	23	Note A	173.0-173.5	...	I, 173	...	...
Phenylethylene	24	SD, 2Dc	...	-33.3	...	69.5-70 (60 mm.)	1.0
1,1-Diphenylethylene	25	D, 2Dc	...	8.2	I, 9	94-95 (1 mm.)	0.7
1,2-Diphenylethylene	26	D, 3Ca, D, 2Ca	124.5-124.8	123.9	I, 124	...	.5
Triphenylethylene	27	D, 6Ca	69.0-69.5	65.8	B, 62, 68	...	...
Tetraphenylethylene	28	6Cb	224.6-224.9	224.7	I, 221	...	1.1
Phenylacetylene	29	3D, Dc	...	-44.8	...	142-143, I, 143	1.0
Diphenylacetylene	30	Note B	59-61	...	...	...	...
Benzylchloride	E. K. Co.	4Dc	...	61.6	I, 60	...	...
Diphenylchloromethane	31	D, Dc	...	-39.7	I, -39	178.5 (754 mm.)	0.5
Triphenylchloromethane	E. K. Co.	...	106-110	17.0	B, 12-14	113-114 (1.5 mm.)	1.5
Benzyl alcohol	E. K. Co.	...	...	109.2	I, 112	...	2.5
Diphenylcarbinol	E. K. Co.	...	64-65	-16.0	I, -15.3	85-85.5 (7 mm.)	1.0
Triphenylcarbinol	32	4Cb	162.4-162.5	162.2	I, 68	...	2.0
					I, 162.5	...	0.1

NOTE A.—This compound was prepared according to the directions of Gomberg and Cone from diphenylbromomethane and triphenylchloromethane by treatment with magnesium activated with iodine. Solution in benzene and precipitation with alcohol several times failed to remove the triphenylcarbinol present. The compound was then twice dissolved in benzene and precipitated with petroleum ether. After this treatment the product gave only a slight yellow color with concd. sulfuric acid, indicating the presence of only a trace of triphenylcarbinol.

NOTE B.—Stilbene in ether solution was treated with bromine and the resulting stilbene dibromide was easily effected by this treatment, but the second required potassium hydroxide solution. The removal of the first hydrogen bromide under reduced pressure and recrystallized six times from alcohol. Prolonged boiling of the mixture. The diphenylacetylene was distilled under reduced pressure and recrystallized twice from alcohol. The melting point was then two degrees lower than that given in the literature. Diphenylacetylene picrate was prepared and twice recrystallized from alcohol. The picrate was decomposed with dilute sodium hydroxide solution, and the hydrocarbon taken up in benzene and washed free of sodium picrate. The diphenylacetylene which had been through this process was finally recrystallized twice with alcohol.

The first three members of this series were compounds of unusual purity, and the tetraphenylmethane used, while perhaps not quite so pure, melts too high for this to have had an appreciable effect on the results. The

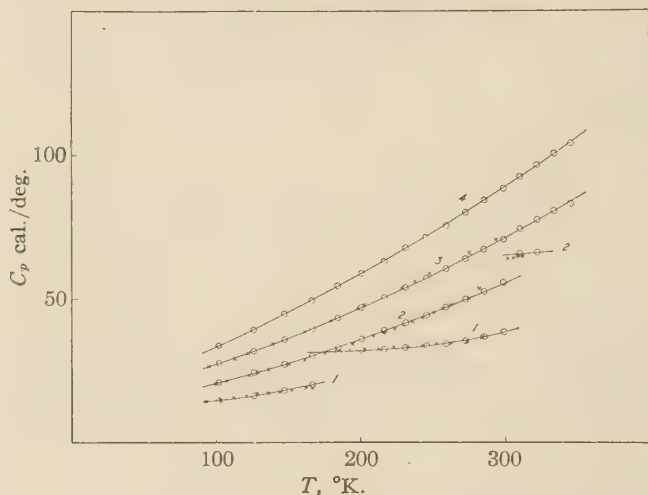


Fig. 1.—Molal heat capacities of the phenyl substituted methanes: 1, toluene; 2, diphenylmethane; 3, triphenylmethane; 4, tetraphenylmethane. The X's indicate results obtained on toluene by Kelley and those on diphenylmethane and triphenylmethane by Huffman, Parks and Daniels.

¹⁴ Friedel and Balsohn, *Bull. soc. chim.*, [2] **33**, 337 (1880).

¹⁵ "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. IV, pp. 81-83.

¹⁶ Ullman and Munzhuber, *Ber.*, **36**, 404 (1903).

¹⁷ Klages and Heilmann, *ibid.*, **37**, 1449 (1904).

¹⁸ Cannizzaro and Rossi, *Compt. rend.*, **53**, 541 (1861); *Ann.*, **121**, 250 (1862); Stelling and Fittig, *ibid.*, **137**, 258 (1866).

¹⁹ Gomberg and Cone, *Ber.*, **39**, 1466, 2963 (1906).

²⁰ Klages and Heilmann, *ibid.*, **37**, 1455 (1904).

²¹ Gomberg and Cone, *ibid.*, **39**, 1463 (1906).

²² Norris, Thomas and Brown, *ibid.*, **43**, 2959 (1910).

²³ Gomberg and Cone, *ibid.*, **39**, 1467 (1906).

²⁴ "Organic Syntheses," 1928, Vol. VIII, pp. 84-86.

²⁵ "Organic Syntheses," 1926, Vol. VI, pp. 32-34.

²⁶ Hell, *Ber.*, **37**, 453 (1904).

²⁷ Hell and Wiegandt, *ibid.*, **37**, 1431 (1904).

²⁸ Engler and Bethge, *ibid.*, **7**, 1128 (1874); Boissieu, *Bull. soc. chim.*, [2] **49**, 681 (1888); Nef, *Ann.*, **298**, 237 (1897).

²⁹ Hessler, "Organic Syntheses," 1922, Vol. II, pp. 67-69.

³⁰ Fittig, *Ann.*, **168**, 74 (1873).

³¹ Boeseken, *Rec. trav. chim.*, **22**, 312 (1903); Montagne, *ibid.*, **25**, 404 (1906).

³² Acree, *Ber.*, **37**, 2755 (1904).

purity of the compounds, together with the fact that three of them have recently been studied by other investigators, makes this series the best check obtained on the method. Three runs were made on toluene and the mean of the best two taken for the final values. The results for triphenylmethane represent the mean of three runs on different weights.

Kelley³³ has made very careful determinations of the heat capacity of toluene from 17°K. to room temperature. The mean deviation of thirteen points from a curve through his results was 1.3%. Huffman, Parks and Daniels² have studied diphenylmethane and triphenylmethane. The mean deviation from their results was 0.9% for the first and 1.3% for the second compound. These deviations are not consistently in one direction. With both compounds the curves for the two sets of results cross once. Their results for diphenylmethane are, in general, lower and for triphenylmethane higher than those obtained in this work.

The heat capacity increment for a phenyl group in the series is practically constant at low temperatures. At higher temperatures the increment between the third and fourth members is somewhat larger than between the second and third. Unfortunately, the errors in the determinations may be accumulated in these increments and make any conclusions that may be drawn from a few compounds rather uncertain. The heat capacity of the phenyl group will be discussed further in considering the other series.

Heat Capacities of the Phenyl Substituted Ethanes.—With the possible exception of 1,1-diphenylethane, the purity of the materials for this series

TABLE IV
MOLAL HEAT CAPACITIES OF THE PHENYL SUBSTITUTED ETHANES

T, °K.	Ethyl- benzene	1,1- Diphenyl- ethane	1,2- Diphenyl- ethane	1,1,1- Triphenyl- ethane
	Calories per degree			
101.9	16.7	22.9	23.4	28.9
126.1	19.4	26.5	26.8	33.6
147.4	21.7	29.6	29.9	38.3
166.7	23.5	32.7	33.0	42.4
	Liquid			
184.4	36.3	35.4	36.0	46.6
201.1	37.3	38.7	39.1	50.7
216.8	38.0	41.8	42.1	54.6
231.7	38.7	44.8	45.0	58.1
246.0	39.8	Liquid	48.1	61.8
259.8	41.0	65.0	51.3	65.4
273.1	41.9	67.2	54.3	69.0
286.0	43.0	68.8	57.5	72.2
298.5	43.9	70.5	60.6	75.7
310.7				78.9
322.6				81.8
334.3				84.7
345.7				87.7

³³ Kelley, *J. Am. Chem. Soc.*, **51**, 2738 (1929).

TABLE V
MOLAL HEAT CAPACITIES OF THE PHENYL SUBSTITUTED ETHANES

T, °K.	1,1,2-Triphenyl-ethane	1,1,1,2-Tetraphenyl-ane	1,1,2,2-Tetraphenyl-ethane	Penta-phenyl-ethane
	Calories per degree			
101.9	29.0	35.4	36.7	43.0
126.1	34.2	41.7	42.7	50.1
147.4	39.0	47.0	48.4	56.3
166.7	43.3	51.8	53.4	62.2
184.4	47.7	57.1	58.7	68.0
201.1	51.4	62.0	63.9	74.2
216.8	55.1	67.3	68.4	80.4
231.7	58.7	71.7	72.9	85.9
246.0	62.3	76.2	77.4	91.5
259.8	65.8	81.1	82.2	97.0
273.1	69.2	85.8	86.9	102.5
286.0	72.7	90.1	91.0	107.8
298.5	76.4	94.5	94.8	113.2
310.7	80.2	98.9	98.4	119.3
322.6		103.0	102.1	124.1
334.3		107.5	106.0	128.1
345.7		111.6	110.0	130.5

left little to be desired. The last point for solid 1,1-diphenylethane was taken from the extrapolated Q/θ curve.

Huffman, Parks and Daniels² have also measured the specific heats of ethylbenzene and 1,2-diphenylethane. The mean deviations from their results are 1.5 and 1.4%, respectively, their results being, for the most part, higher.

The phenylethane series contains three pairs of isomers of a type not previously studied. The results indicate that the heat capacity of the more symmetrical isomer is higher in each case. However, the differences are of the order of the experimental error and more accurate measurements would be desirable for these compounds. Runs were made on the two tetraphenylethanes in May, 1929, and again in February, 1930. Differences of the same order were found on both occasions. The runs on the other pairs of isomers have not been repeated. In the case of the triphenylethanes, it is difficult to say which is the more symmetrical. The higher melting point of 1,1,1-triphenylethane would indicate greater symmetry for that compound. However, the heat capacity of 1,1,2-triphenylethane is slightly higher than that of 1,1,1-triphenylethane. With the three pairs of isomers it is, perhaps, better to say that there is an indication of slightly higher heat capacities for the isomers having the more even distribution of the phenyl groups around the ethane C-C bond.

The increments for the phenyl groups are surprisingly constant for the symmetrical and for the unsymmetrical members of the series. The differences are, of course, more irregular if taken between a symmetrical and an unsymmetrical member. As in the phenylmethane series, there is a slight

indication that the increment for the phenyl group is greater between the higher members of the series. The data obtained are tabulated in Tables IV and V and shown graphically in Fig. 2.

Heat Capacities of the Phenyl Substituted Ethylenes.—The increment for the phenyl group in this series is fairly constant for a given temperature and is about the same as found for the methanes and ethanes. The heat capacities of the ethylenes are slightly lower, especially at higher temperatures, than those of the corresponding ethanes. This might be attributed

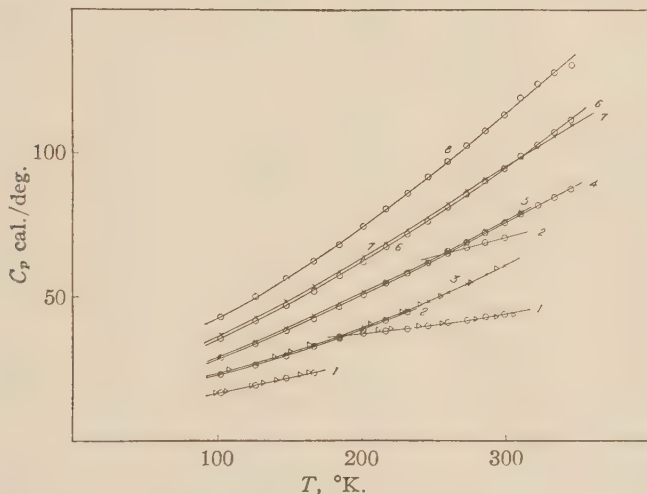


Fig. 2.—Molal heat capacities of the phenyl substituted ethanes: 1, ethylbenzene; 2, 1,1-diphenylethane; 3, 1,2-diphenylethane; 4, 1,1,1-triphenylethane; 5, 1,1,2-triphenylethane; 6, 1,1,1,2-tetraphenylethane; 7, 1,1,2,2-tetraphenylethane; 8, pentaphenylethane. The triangles show the data obtained by Huffman, Parks and Daniels on ethylbenzene and 1,2-diphenylethane.

to the greater strength of the double bond, but, since these differences are only about 2 or 3% at 300°K., such a conclusion would be quite uncertain. It will be observed that the results for 1,1-diphenylethylene are appreciably higher than for the symmetrical isomer. This is the reverse of what was found for the ethanes.

With the exception of phenylethylene, the purity of the materials used for the determinations in this series was satisfactory. Marked premelting of the phenylethylene made it impossible to obtain any results over a considerable range below the melting point. In fact, the accuracy of all the data on this compound is questionable.

Table VI shows the results for the phenyl compounds of ethylene.

Heat Capacities of the Phenyl Substituted Acetylenes.—The data are given in Table VII. There being only two members of this series, fewer

comparisons can be made. The phenyl group increment is about the same as was found for the three foregoing sets of compounds. The heat capacity of diphenylacetylene at higher temperatures is slightly lower than that of the corresponding ethylene. Here again the difference is in the direction expected, but it is scarcely greater than the possible error in the measurements.

TABLE VI
MOLAL HEAT CAPACITIES OF THE PHENYL SUBSTITUTED ETHYLENES

T, °K.	Phenyl- ethylene	1,1- Diphenyl- ethylene	1,2- Diphenyl- ethylene	Triphenyl- ethylene	Tetraphenyl- ethylene
	Calories per degree				
101.9	15.6	22.3	21.8	29.1	37.0
126.1	18.9	26.3	25.4	33.9	43.0
147.4	21.9	29.8	28.8	38.1	48.6
166.7	24.5	33.3	32.0	42.3	53.2
184.4	..	36.6	35.1	46.4	58.1
201.1	..	39.4	38.1	50.5	63.2
216.8	..	42.2	40.8	54.5	67.6
231.7	Liquid	44.9	43.1	57.3	71.6
246.0	39.7	47.7	45.6	60.6	75.6
259.8	40.4	50.7	48.1	63.9	79.8
273.1	41.1	Liquid	50.8	67.3	83.5
286.0	41.9	70.1	53.1	70.4	87.8
298.5	43.0	71.5	55.6	73.9	92.5
310.7			58.1	77.5	96.4
322.3			60.3	80.7	100.3
334.3			62.6		103.8
345.7			64.5		107.2

TABLE VII
MOLAL HEAT CAPACITIES OF THE PHENYL SUBSTITUTED ACETYLENES

T, °K.	Phenyl- acetylene Calories per degree	Diphenyl- acetylene Calories per degree	T, °K.	Phenyl- acetylene Calories per degree	Diphenyl- acetylene Calories per degree
101.9	15.0	21.7	231.7	Liquid	
126.1	17.3	24.8	246.0	38.9	42.2
147.4	19.4	28.0	259.8	39.5	44.5
166.7	21.4	31.3	273.1	40.0	47.0
184.4	23.3	34.3	286.0	40.7	49.2
201.1	25.1	37.2	298.5	41.7	51.6
216.8	26.9	39.7	310.7	42.9	54.0
			322.6		56.4
					58.5

Heat Capacities of the Phenyl Carbinols.—Of the three compounds in this series, only the triphenylcarbinol was obtained in a state of really satisfactory purity for thermal measurements. With benzyl alcohol a small "hump" was observed in the Q/θ curve between 150° and 200°K. The readings appeared to be normal above and below this region and the

heat capacity was calculated from a smooth curve which disregarded the irregular points. It seemed quite probable that these were due to the melting of a small amount of impurities.

TABLE VIII
MOLAL HEAT CAPACITIES OF THE PHENYL CARBINOLS

T, °K.	Benzyl alcohol	Diphenylcarbinol Calories per degree	Triphenylcarbinol
101.9	14.6	21.2	29.2
126.1	17.5	25.0	34.5
147.4	20.1	27.7	39.1
166.7	22.2	31.3	43.6
184.4	24.2	34.3	47.8
201.1	26.1	37.4	51.7
216.8	27.9	40.3	55.4
231.7	29.7	42.9	59.0
246.0	Liquid	45.7	62.5
259.8	45.3	48.2	66.1
273.1	47.9	50.8	69.6
286.0	49.9	53.7	72.9
298.5	51.6	56.6	76.2
310.7			79.4
322.6			82.4
334.3			85.1
345.7			87.7

The heat capacity increment between di- and triphenylcarbinol over the whole temperature range is consistently 2 to 3 calories higher than it is between diphenylcarbinol and benzyl alcohol.

The data are represented in Table VIII.

TABLE IX
MOLAL HEAT CAPACITIES OF THE PHENYLCHLOROMETHANES

T, °K.	Benzyl chloride	Diphenylchlormethane	Triphenylchlormethane
		Calories per degree	
101.9	17.3	23.6	29.5
126.1	19.7	26.8	34.8
147.4	22.2	29.8	39.3
166.7	24.5	32.8	43.2
184.4	26.7	35.6	47.2
201.1	28.8	38.4	51.0
216.8	..	41.2	55.0
231.7	Liquid	43.5	58.3
246.0	41.4	46.3	61.6
259.8	42.1	49.2	64.6
273.1	42.5	51.8	67.7
286.0	43.1	Liquid	70.9
298.5	43.6	69.4	74.5
310.7		70.7	78.1
322.6			80.9
334.3			83.4
345.7			85.3

Heat Capacities of the Phenylchloromethanes.—The differences in the heat capacities between the second and third members of the series is 2 or 3 calories greater than that between the first and second. This is again in the direction that would be expected if the valence force between carbon and chlorine is decreased with the addition of the phenyl groups.

Unfortunately, the purity of the materials used for measurements in this series was not so good. The benzyl chloride was the best of the three. Table IX gives the results obtained.

Conclusions

The conclusions to be drawn from the data reported here fall naturally into two groups, those of thermodynamic interest such as the calculation of entropy, and free energy, and those of kinetic interest such as the study of the distribution of thermal energy among the different parts of a molecule. Since it is necessary in making the thermodynamic calculations to extrapolate the curves to absolute zero, these calculations will not be discussed until the new methods of extrapolation based on Raman spectra have been presented in a later paper. The conclusions of kinetic interest are also closely related to the structure of the molecule as revealed by Raman spectra, but in connection with them it is perhaps worth while to point out a few facts of general significance which may be deduced directly from the data.

One of the principal reasons for the study of this series lies in the hope that some light may be thrown on the change in the ethane carbon-carbon bond which seems to take place, according to the chemical evidence, as we load down the molecule with phenyl groups. From the fact that in triphenylmethyl this carbon-carbon bond is completely severed, we might expect that a progressive weakening would take place as we go down the series. If this were true, there should be a decrease in the frequency of vibration of all the types of motion which involve this bond and the heat capacity due to such vibrations should be increased.

The easiest way to look for such an effect, without making a careful analysis of all the terms involved (as will be done later), is to look for a change in the increment in heat capacity caused by the addition of a phenyl group as we proceed down the series. It is true that if the addition of each succeeding phenyl group caused the same increase in loosening of the carbon-carbon bond, the increments in heat capacity might be the same for each successive addition and the effect would be masked. However, since the frequency (ν) varies as the square root of the force constant (k) of the bond

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (1)$$

(μ is a function of the mass) and since the specific heat is an exponential

function of the frequency, such an effect is hardly to be expected. Moreover, we can compare the increment due to the phenyl group in the ethane series to the increment in the methane and other series where there is no possibility of a similar loosening effect.

Table X shows the increments in heat capacity which are found between different members of the two series. The approximate constancy of the increment at any given temperature is at once apparent. There is only a slight tendency for it to increase appreciably toward the end of the series, and it is essentially the same in all the different series. This seems to point definitely to the fact that the force constant of the bond is not greatly affected and that the heat capacity of the phenyl radical is quite independent of its environment in these groups.

This, of course, does not prove that the *breaking* of the carbon-carbon bond is not rendered easier by phenylation. Since the strength of the bond is defined in so many different ways, a word may perhaps be in order to distinguish clearly the difference between the *force constant* or *elastic constant* and the *chemical strength* or *heat of linkage*. Figure 3 shows the way the force of a single normal bond varies with the separation of the two carbon atoms which it joins.³⁴ When they are 1.5 Å. apart, equilibrium

TABLE X
HEAT CAPACITY INCREMENTS FOR ADDITION OF A PHENYL GROUP, CAL./DEG.

	120°	220°	320°
Toluene	7.5	..	..
Diphenylmethane	7.5	11.6	...
Triphenylmethane	7.1	12.9	19.0
Tetraphenylmethane			
Ethylbenzene	6.8	..	..
1,1-Diphenylethane	7.2	12.9	..
1,1,1-Diphenylethane	7.3	12.9	21.0
1,1,1,2-Tetraphenylethane	8.0	13.4	20.3
Pentaphenylethane			
Ethylbenzene	7.2	..	..
1,2-Diphenylethane	7.2	13.0	..
1,1,2-Triphenylethane	8.1	13.8	..
1,1,2,2-Tetraphenylethane	6.8	12.1	21.0
Pentaphenylethane			
Phenylethylene	7.3	..	..
1,1-Diphenylethylene	7.4	12.4	..
Triphenylethylene	8.9	13.3	19.6
Tetraphenylethylene			
Phenylethylene	6.3	..	..
1,2-Diphenylethylene	8.3	13.8	20.3
Triphenylethylene			
Phenylacetylene	7.3	12.9	..
Diphenylacetylene			

³⁴ D. H. Andrews, "Colloid Symposium Annual," 1930, p. 119.

distance, there is no force acting between them. Closer than this they are repelled; further apart, they are attracted with a force which, however, goes through a maximum and becomes practically zero as the distance between them is increased to the point where they are "dissociated." Now the vibrations which determine the heat capacity in the case we have been

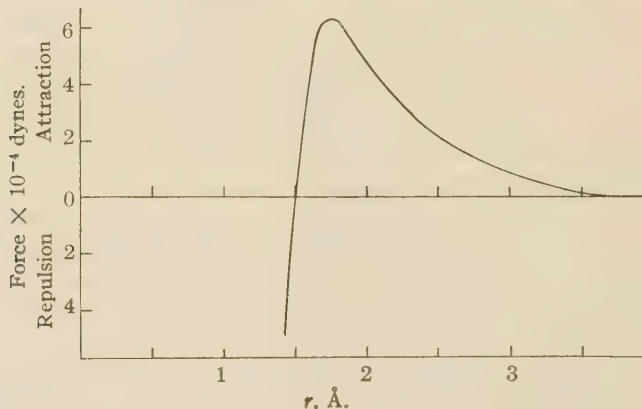


Fig. 3.—The force of a single homopolar bond operating between two carbon atoms separated by distance r , according to the Morse wave mechanics function (Ref. 35).

studying take place with an amplitude of only a few tenths of an $\text{\AA}$. about the equilibrium position. The force constant (k) in Equation 1 is the slope of the curve in Fig. 3 in the neighborhood of the equilibrium position. We can, therefore, say that in the normal state of the molecule, at the temperatures considered, phenylation has not greatly affected the bond in respect to its *force constant*. As regards chemical activity, however, it is evident from the figure that to pull the molecule to pieces and form a new chemical compound, one must overcome the force in the region of the maximum and beyond. We can get evidence about the nature of this part of the curve from the heat of dissociation, since the latter is the integral represented by the area under the curve from the equilibrium point to dissociation, that is, where the force drops to zero again. There is reason to believe that the heat of dissociation does fall off with increasing phenylation. In other words, as we pull the molecule apart and distort the electron configuration, we find phenylation has a decided effect on molecular behavior, although in the undistorted molecule the addition of phenyl groups does not seem to affect the ethane C-C linkage.

These conclusions are in accord with the idea that the normal homopolar chemical bond is a definite structural unit and that its properties are relatively independent of the nature of the atoms which it joins or the other atoms near it, if the atomic weights are not higher than about twenty.

This concept of the bond first took concrete form in Lewis's suggestion that the bond is made up of a pair of electrons. The quantitative evidence from spectra and heat capacities substantiates this hypothesis^{7,8} and the results presented here seem to be in good agreement with it.

Summary

1. The accuracy of the measurement of heat capacity by the method of calibrated heat conduction has been improved.
2. The heat capacities of phenyl derivatives of methane and ethane and thirteen related compounds have been measured from 100 to 320°K.
3. An analysis of the data indicates that in the normal or unexcited molecule there is very little decrease in the force of the ethane carbon-carbon bond upon phenylation. This favors the idea that the bond is a definite structural unit relatively independent of its environment.

II. PHENYL DERIVATIVES OF METALS

In planning the study of thermal energy in phenyl derivatives as outlined in the previous paper of this series,¹ it seemed desirable to include some compounds which would introduce other variables than those found in the purely organic molecules. Of the many compounds available, the phenyl derivatives of the metals are almost ideally fitted for this purpose because a change in the central metal atom presumably brings about a change in the size of the molecule and in the separation of the phenyl groups, as well as a change in the valence force. Accordingly there were obtained fourteen phenyl derivatives of various metals and elements closely related to them and the specific heats were measured by the method described in the first paper of this series.

Preparation of Materials

The same general procedure for preparation and purification was followed as described in the first paper of this series.¹ The meaning of the symbols used below may be found in that paper.¹

Triphenylamine.—The Eastman Kodak Company product was used as received.—m. p.: M. T., 126.5°; T. C., 125.8°; I. C. T., 126.5°; T. T. C., 0.2% (impurities estimated from time-temperature curves).

Triphenylphosphine.—The Eastman Kodak Company product was used as received.—m. p.: M. T., 77–77.5°; T. C., 74.7°; I. C. T., 79°; T. T. C., 2%. This value is doubtful because the temperature does not rise to the melting point when the compound freezes. The triphenyl compounds of the elements of the fifth group apparently have quite low heats of fusion.

Triphenylarsine.—The Eastman Kodak Company product was used as received.—m. p.: M. T., 59–59.3°; T. C., 56.4°; I. C. T., 60°; T. T. C., 1% (see triphenylphosphine).

Triphenylstibine.—The Eastman Kodak Company product was used as received.—

¹ Richard H. Smith and Donald H. Andrews, *J. Am. Chem. Soc.*, **53**, 3644 (1931).

m. p.: M. T., 51.5–52.5°; T. C., 48.0°; I. C. T., 48°; T. T. C., 1.5% (see triphenylphosphine).

Triphenylbismuthine.—This compound was prepared at the University of Illinois and was used as received.—m. p.: M. T., 76.5–77.5°; T. C., 73.5°; I. C. T., 78°; T. T. C., 2.0% (see triphenylphosphine).

Mercury Diphenyl.—Dr. Parry Borgstrom, of the Naval Research Laboratory, Washington, D. C., prepared this compound and it was used as received.—m. p.: M. T., 124–125°; S. (1912–1913), 121.8°; S. (1916–1918), 120–123°. (S. refers to Stelzner's, "Literatur Register der organische Chemie.")

Mercury Di-(*p*-tolyl).—The Eastman Kodak Company preparation was used as received.—m. p.: M. T., 238–239°; B., 232–233°.

Tetraphenylsilicane.²—This was prepared by treating bromobenzene and silicon tetrachloride in ether solution with sodium. It was three times recrystallized from benzene.—m. p.: M. T., 233–235°; S. (1912–1913), 233°.

Tetraphenyl Tin.—This compound was prepared by Dr. Parry Borgstrom and was used as received.—m. p.: M. T., 225.5–226.5°; S. (1919–1921), 226°.

Diphenyl oxide supplied by the Dow Chemical Works was fractionated through the column.—b. p. 83–84° at 1 mm.; m. p.: M. T., 26.6–26.9°; T. C., 26.75°; I. C. T., 26.9°; T. T. C., 0.5%.

Diphenyl Sulfide.—The Eastman Kodak Company preparation was used as received.—m. p.: M. T., –25.9°; T. T. C., 2.5%.

Diphenyl Sulfoxide.—The Eastman Kodak Company product was used as received.—m. p.: M. T., 68–70°; T. C., 69.4°; I. C. T., 70.5°; T. T. C., 0.8%.

Diphenyl Sulfone.—The Eastman Kodak Company product was used as received.—m. p.: M. T., 128–128.5°; T. C., 127.2°; I. C. T., 129°; T. T. C., 1.0%.

TABLE I

MOLAL HEAT CAPACITIES OF PHENYL
AND TOLYL SUBSTITUTED MERCURY

T, °K.	Mercury diphenyl Calories	Mercury di- <i>p</i> -tolyl per degree
101.9	23.8	30.5
126.1	27.2	34.9
147.4	30.1	38.4
166.7	32.8	41.7
184.4	35.5	44.3
201.1	38.3	47.4
216.8	40.9	50.0
231.7	43.2	52.3
246.0	45.4	54.6
259.8	47.3	56.3
273.1	49.5	58.2
286.0	51.7	60.2
298.5	53.9	62.7
310.7	56.1	65.5
322.6	58.2	67.7
334.3	60.4	70.1
345.7	62.4	71.9

TABLE II

MOLAL HEAT CAPACITIES OF THE TETRA-
PHENYL COMPOUNDS OF ELEMENTS IN THE
FOURTH GROUP OF THE PERIODIC TABLE

T, °K.	Tetra- phenyl- methane Calories	Tetra- phenyl- silicane per degree	Tetra- phenyl tin
101.9	33.9	41.8	42.0
126.1	39.4	47.6	49.1
147.4	44.7	53.3	55.3
166.7	49.6	58.6	60.7
184.4	54.7	62.8	65.9
201.1	59.1	68.2	71.0
216.8	63.0	73.7	75.6
231.8	67.7	77.0	79.8
246.0	71.4	81.1	84.6
259.8	75.4	83.4	89.1
273.1	79.9	87.0	93.4
286.0	84.0	90.3	97.4
298.5	88.0	94.6	101.9
310.7	92.2	101.0	106.3
322.6	96.4	105.4	110.0
334.3	100.2	110.5	113.4
345.7	103.8	114.1	116.2

² Polis, *Ber.*, 18, 1542 (1885); Kipping and Lloyd, *J. Chem. Soc.*, 79, 451 (1901).

Results

The data for the different compounds are presented in Tables I, II, III and IV and in Figs. 1 and 2. The curves are of the same general type as those of purely organic molecules and there does not appear to be

TABLE III

MOLAL HEAT CAPACITIES OF THE TRIPHENYL COMPOUNDS OF ELEMENTS IN THE FIFTH GROUP OF THE PERIODIC TABLE

T, °K.	Triphenyl- amine	Triphenyl- phosphine	Triphenyl- arsine	Triphenyl- stibine	Triphenyl- bismuthine
	Calories per degree				
101.9	27.1	28.4	30.5	35.3	35.3
126.1	31.8	33.3	35.8	39.6	40.2
147.4	36.3	37.6	40.3	44.5	44.8
166.7	40.1	41.2	44.5	48.6	49.3
184.4	44.1	45.0	48.5	52.3	52.6
201.1	48.0	48.4	52.2	56.3	56.8
216.8	51.5	52.0	56.2	61.1	60.9
231.7	55.0	55.8	59.8	63.8	64.2
246.0	58.2	60.1	63.2	66.7	67.2
259.8	61.4	64.1	70.9	73.4	75.1
273.1	64.6	67.6	69.6	70.5	72.1
286.0	67.9	70.9	72.9	73.4	75.1
298.5	71.1	74.7	76.8	77.8	78.5
310.7	74.1		80.7	83.3	82.3
322.6	77.1				85.0
334.3	79.8				
345.7	82.2				

TABLE IV

MOLAL HEAT CAPACITIES OF DIPHENYL OXIDE, DIPHENYL SULFIDE AND THE OXIDATION

PRODUCTS OF DIPHENYL SULFIDE

T, °K.	Diphenyl oxide	Diphenyl sulfide	Diphenyl sulfoxide	Diphenyl sulfone
	Calories per degree			
101.9	20.3	22.3	23.3	24.1
126.1	23.6	26.0	27.3	28.1
147.4	26.5	29.5	30.7	31.7
166.7	29.3	32.7	33.6	34.6
184.4	31.9	35.8	36.6	38.0
201.1	34.8	..	39.6	40.9
216.8	37.4	..	42.4	44.0
231.7	39.8	..	45.1	46.5
246.0	42.2	Liquid	47.6	49.1
259.8	44.3	61.5	50.3	51.6
273.1	46.8	62.3	52.5	53.8
286.0	49.0	63.5	54.7	56.0
298.5	51.6	64.8	57.3	58.4
310.7			60.0	60.8
322.6			62.7	62.9
334.3				64.9
345.7				66.7

any unusual heat of transition or other thermal phenomenon. It may readily be seen, however, that the nature of the central metal atom has a de-

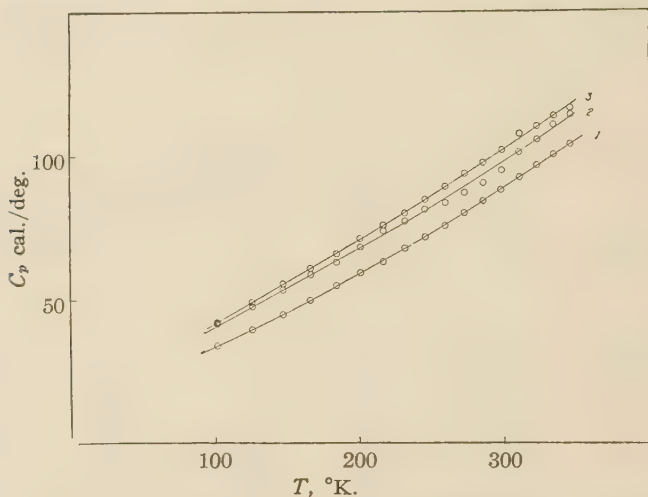


Fig. 1.—Molal heat capacities of the tetraphenyl compounds of elements in the fourth group of the periodic table: 1, tetraphenylmethane; 2, tetraphenylsilicane; 3, tetraphenyl tin.

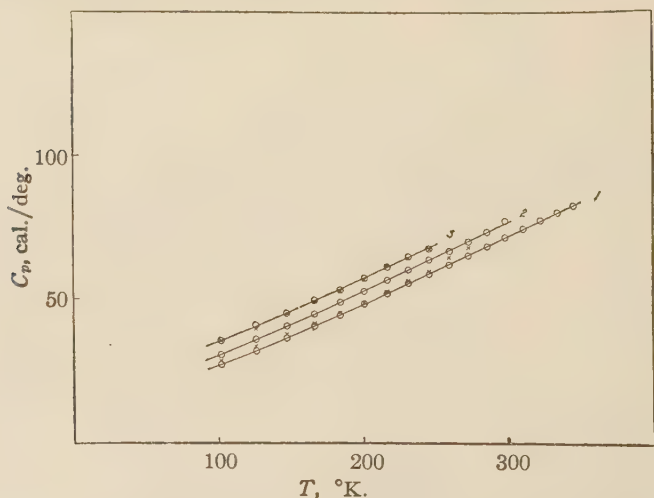


Fig. 2.—Molal heat capacities of the triphenyl compounds of elements in the fifth group of the periodic table: 1, triphenylamine—the X's along this curve are for triphenylphosphine; 2, triphenylarsine; 3, triphenylbismuthine—the X's are for triphenylstibine.

cided effect on the heat capacity. This is particularly noticeable in the series containing elements from the fifth group of the periodic table. The

tendency is for the heat capacity to increase with increasing atomic weight, but in proceeding from the amine to the phosphine, or from the stibine to the bismuthine, the additional weight does not appear to have any effect.

There are three ways in which one might expect the heat capacity to be affected by the change in the central atom. In the first place, an increase in weight would lower the frequency of vibration, which in turn would increase the heat capacity since the vibration is definitely quantized for nearly all the motions which primarily involve the central atom. In the second place, changing the central atom may mean an increase in the volume of the molecule which in turn may result in greater freedom of motion of the phenyl groups, and consequent increase in heat capacity. Thirdly, changing the central atom may mean a change in the strength of the bonds which tie the phenyl groups to the central atom, and this might well vary the heat capacity throughout the entire molecule.

In order to observe more clearly the evidence for these effects, a table has been prepared which presents that part of the heat capacity of each molecule which remains when the heat capacities of the phenyl groups have been subtracted. As may be seen in the previous paper,¹ the addition of a phenyl group adds the same amount to the heat capacity of the molecule, in nearly all cases. Averaging the increments found in the study of the hydrocarbons, we can take this value, multiply it by the numbers of phenyl groups present, and subtract the result from the observed heat capacity at any given temperature. This gives us a value which represents roughly the part of the heat capacity due to the central atom and to the motion of the molecule as a whole in the crystal lattice. Calculations of this sort have been made for three temperatures and the results are given in Table V.

TABLE V
CALCULATED COMPARATIVE DATA

Central atom	At. wt.	θ	C_v , calculated for central atom			C_p , excess over phenyl groups		
			126.1°K.	216.8°K.	322.6°K.	126.1°K.	216.8°K.	322.6°K.
C	12	1560	0.0	0.2	1.1	8.6	12.6	14.8
Si	28	1030	0.1	1.2	2.7	16.8	23.3	23.8
Sn	119	500	1.8	3.9	5.0	18.3	25.2	28.4
N	14	1450	0.0	0.4	1.4	8.7	13.7	14.9
P	31	970	0.2	1.5	3.0	10.2	14.2	..
As	74	620	1.1	3.2	4.4	12.7	18.4	..
Sb	120	490	1.9	4.0	5.0	16.5	23.3	..
Bi	208	370	3.0	4.7	5.4	17.1	23.1	23.8

In order to get an idea of the change in heat capacity due to the increase in weight, another series of calculations has been made. Our molecule is made up of the central metal atom surrounded in space by the phenyl groups attached to it. In the case of three- or four-valent metals the principal forces which restrain the motion of the central atom will be the

homopolar bonds which link it to the phenyl groups. As a first approximation we may regard the resultant of these forces as producing a restoring force which will be practically the same for any direction of motion of the central atom. The movements at the central atom will therefore approximate harmonic vibrations in the three directions in space and will have a single common frequency.

In order to ascertain the effect of weight as distinguished from that due to change in bond strength, let us assume for the moment that the bonds in all these molecules will have the same elastic constant (k) as the normal homopolar bond between two carbon atoms. From a knowledge of the mass of the atom (m) we can then calculate the frequency of vibration (ν) from the formula

$$\nu = \frac{1}{2\pi} \sqrt{\frac{nk}{m}} \quad (1)$$

where n will be the average number of bonds which are effective for any displacement of the central atom. For the cases we are considering here, three- and four-valent atoms with the bonds uniformly distributed in space, n will probably have a value of about two. In this way the frequency of vibration of the metal atom has been calculated for eight of the compounds. Since it is customary in specific heat calculations to use the characteristic temperature θ which is equal to $h\nu/k$ (h , Planck's constant; k , Boltzmann's constant), the values of θ rather than of ν have been given in Table V.

From these the heat capacity due to the vibrations of the central atom can easily be calculated with the help of Einstein's formula for the heat capacity of an harmonic oscillator.³ Such values for three different temperatures are also given in Table V.

It may readily be seen that the increase in heat capacity due to this effect is not nearly large enough in most instances to account for the observed increase in heat capacity. Of course there may be other types of motion in the molecule for which increasing weight would change the heat capacity, but we might expect such a change to be more in the nature of a second order effect.

The change in heat capacity from carbon to silicon is perhaps the most striking in the whole group. This suggests the second effect which was mentioned above, namely, that due to the increase in the size of the central atom. It seems reasonable to suppose that in tetraphenylmethane the four phenyl groups are drawn in so close to the central carbon atom that their motions toward and away from each other are restricted to a considerable extent by their mutual fields of force. We would expect, then, as we pass to a larger central atom that this crowding would be eliminated, and

³ See W. Nernst, "New Heat Theorem," E. P. Dutton, New York, for tables to simplify the calculation.

that an increase in heat capacity would result, say, in passing from carbon to silicon, an increase which would become less marked in higher members of the series. This is certainly true as we pass from silicon to tin. Unfortunately data are not available for the densities of these compounds.

On the other hand, if we compare the tetravalent with the trivalent series we are immediately struck by the fact that the residue of heat capacity due to the central atom and to the molecule as a whole is almost identical for carbon and nitrogen. If the three bonds of nitrogen lie at approximately right angles to each other as Slater⁴ has deduced from wave mechanics, the crowding of phenyl groups might be just as great as in the case with carbon at the center. However, as we proceed along this series we find no striking increase in heat capacity like that experienced in going from carbon to silicon. This suggests that the increase in heat capacity is due to a weakening of the bonds. The fact that tetraphenyl tin has been used as a phenylating agent,⁵ while tetraphenylmethane has no such property, is also evidence in favor of this point of view.

One should also observe in this connection that among the hydrocarbons¹ the constancy of the increment in heat capacity due to a phenyl group when we pass from monophenyl to tetra- or pentaphenyl derivatives is an indication that crowding of the groups is not an important factor. The evidence therefore seems to be strongly in favor of the weakening of the bond forces as we go from low to high atomic weights. This is also in accord with the evidence from spectra in series such as the halogens.⁶ It is hoped that a more careful analysis, such as will be possible when further data from Raman spectra are available, will throw more light on this problem.

Summary

1. The heat capacities of mercury diphenyl, mercury di-*p*-tolyl, tetraphenylmethane, tetraphenylsilane, tetraphenyl tin, triphenylamine, triphenylphosphine, triphenylarsine, triphenylstibine, triphenylbismuthine, diphenyl oxide, diphenyl sulfide, diphenyl sulfoxide and diphenyl sulfone have been measured from 100 to 320°K. by the method of calibrated heat conduction.

2. Evidence is found of a weakening of the binding force between the phenyl groups and the central metal atom, as the weight of the latter increases.

⁴ J. C. Slater, *Phys. Rev.*, **37**, 481 (1931).

⁵ Bost and Borgstrom, *J. Am. Chem. Soc.*, **51**, 1922 (1929).

⁶ J. R. Bates and D. H. Andrews, *Proc. Nat. Acad. Sci.*, **14**, 124 (1928).

BIOGRAPHY

The author of the foregoing dissertation was born at Fincastle, Virginia, October 2, 1901. He attended the public schools of that place and was graduated from the Fincastle High School in 1918. He attended the Mississippi Agricultural and Mechanical College and was graduated from there in 1922, with the degree of Bachelor of Science. In October, 1927, he entered the Johns Hopkins University. During the session of 1927-28 the author held a Hopkins Scholarship, and during the session 1928-29 he held a University Scholarship.

